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**REVIEW AND STUDY OF PHYSICS DRIVEN PITTING
CORROSION MODELING IN 2024-T3 ALUMINUM
ALLOYS (POSTPRINT)**

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Review and Study of Physics Driven Pitting Corrosion Modeling in 2024-T3 Aluminum Alloys

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ABSTRACT

Material degradation due to corrosion and corrosion fatigue has been recognized to significantly affect the airworthiness of civilian and military aircraft, especially for the current fleet of airplanes that have served beyond their initial design life. The ability to predict the corrosion damage development in aircraft components and structures, therefore, is of great importance in managing timely maintenance for the aging aircraft vehicles and in assisting the design of new ones. The assessment of aircraft corrosion and its influence on fatigue life relies on appropriate quantitative models that can evaluate the initiation of the corrosion as well as the accumulation during the period of operation. Beyond the aircraft regime, corrosion has also affected the maintenance, safety and reliability of other systems such as nuclear power systems, steam and gas turbines, marine structures and so on. In the work presented in this paper, we reviewed and studied several physics based pitting corrosion models that have been reported in the literature. The classic work of particle induced pitting corrosion by Wei and Harlow is reviewed in detail. Two types of modeling, a power law based simplified model and a microstructure based model, are compared for 2024-T3 alloy. Data from literatures are used as model inputs. The paper ends with conclusions and recommendations for future work.

Keywords: pitting corrosion, physics based modeling, aluminum alloy, material degradation

1 INTRODUCTION

Performance, reliability, maintainability and life cycle cost of aircraft and other aerospace systems depend to a large extent on the factors that affect the durability of airframe and propulsion system components. Material degradation due to corrosion and corrosion fatigue has been recognized to significantly affect the airworthiness of civilian and military aircraft, especially for the current fleet of airplanes that have served beyond their initial design life (Chen et al., 1997). Aircraft-joints are the most corrosion- and fatigue-susceptible areas on an aircraft (Figure 1). Loads are transferred from one structural detail to another through fasteners. The tight fit of details and fasteners can trap moisture in the joint. Relative movement between the structural details and the fasteners, as well as the stress concentration, can cause corrosion protection systems (anodized Aluminum, primer, and topcoat) to crack and wear, allowing moisture to reach the aluminum parts and affect the corrosion process (Wanhill, 2000). A typical example structure is a longitudinal skin joints on the pressurized fuselage of an aircraft (Ghiocel and Tuegel, 2004). The ability to predict the damage development in aircraft components and structures, therefore, is of great importance in managing timely maintenance for the aging aircraft vehicles, as well as in assisting in the design of new ones. A reliable prediction would largely depend on the quantitative understanding, characterization, and modeling of the process of corrosion and corrosion fatigue.



Figure 1 A B727-100 lap splice sample of internally visible corrosion along the upper side (Wanhill, 2000)

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Corrosion is an important factor that represents one of the Air Force's single largest maintenance cost drivers. Current estimates indicate the detection and repair of corroded aircraft structures costs the Air Force approximately \$3-4 Billion per year (Hermes and Jata, 2012). New nondestructive evaluation (NDE) methods are needed to enable assessment of hard-to-detect corrosion damage. Such tools would allow the Air Force to more effectively manage the fleet by establishing realistic maintenance and upgrade inspection schedule. A quantitative approach for defining suitable inspection intervals and mandating repairs is needed for an effective management of an aging fleet of aircraft (Harlow and Wei, 1994). It is equally important for assessing the durability and structural integrity of airframe components and structures.

The Air Force Corrosion Program Office (AFCPO) has initiated a number of efforts to examine the corrosion problems in the aircraft fleets. Among various forms of corrosion, corrosion fatigue is an important but complex mode of failure for high performance structural metals operating in extreme environments. It involves the conjoint actions of mechanical loading and chemical attack, which can impact the continued safety and availability as well as the cost of operation and sustainment of the systems (Wei and Harlow, 2001). Corrosion fatigue issues are central to the behavior of many fielded and newly acquired AF systems (Hermes and Jata, 2012). Durability of airframes and their components is governed principally by material degradation through localized corrosion, fatigue crack nucleation and growth and corrosion-fatigue (Wei and Harlow, 2001). The assessment of aircraft corrosion and corrosion fatigue relies on appropriate quantitative models that can evaluate the initiation of the corrosion as well as the accumulation during the period of operation. Beyond the aircraft regime, corrosion fatigue has also affected the maintenance costs, safety and reliability of nuclear power systems, steam and gas turbines, marine structures and so on. The outcome of the integrity assessment then can serve as the basis for decision on the life prediction of key structural components across various industries.

Studies on the effects of pitting corrosion on fatigue life that have been undertaken in the past (example: Sankaran and Jata) were mostly based on measuring the maximum pit size and its effect on the fatigue life. Microstructure and corrosion currents were neglected. In this paper we present the literature review of pitting corrosion basics and several modeling approaches in the literature for corrosion fatigue models that incorporate parameters of corrosion environment, microstructural metrics, and corrosion current as well as fatigue loading conditions. The study is based on alloy 2024-T3 and uses data from literature (Sriraman and Pidaparti, 2009).

2 PITTING CORROSION AND FATIGUE

Corrosion in aluminum alloys can be broadly characterized into general corrosion, pitting, exfoliation and intergranular (Ghiocel and Tuegel, 2004). Pitting is a form of localized corrosion that takes the form of cavities on the surface of a metal (such as Figure 2 in Wang et al., 2003). It starts with the local breakdown of protective surface films and may cause the perforation of thin sections, as well as creating stress concentrations that may trigger the onset of fatigue cracking or other types of corrosion. Corrosion of aluminum alloys generally starts with pitting. Isolated pits are difficult to detect, but they have a significant effect on the fatigue life. Pits can occur on boldly exposed surfaces or on the closed cracks. Pits will cause cracks to nucleate faster. As reported by Wei and coworkers, pitting corrosion in aluminum alloys is essentially associated with constituent particles (Chen et al., 1997). Individual particle-induced pits then coalesce to form large pits. The corrosion pits eventually will serve as nucleation sites for subsequent fatigue cracking.

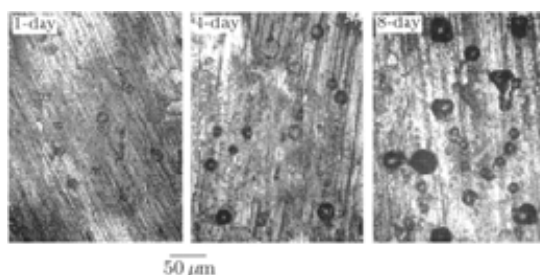


Figure 2 Appearance of the pits on the surface of 7075-T6 (Wang et al., 2003)

The damage being considered in this study is pitting corrosion and its effects on the aluminum alloy fatigue life. Specifically it is motivated by the fact that during service, an aircraft typically experiences corrosion when it is on the ground and fatigue loading during flight. Hence, the crack initiation process in the fatigue life can be replaced with the pitting corrosion model. After the pit is formed, the corrosion has no effect on the fatigue cracking. The corrosion is only the initiator of the fatigue crack. The crack is assumed to grow from the pit from the first loading cycle. Thus, the total life t is given by the sum of the pitting corrosion time t_c and fatigue life t_f with the pre-existing pit:

$$t = t_c + t_f \quad (1)$$

3 PITTING CORROSION MODELING

In this section, we present several pitting corrosion models based on the most accepted Wei and Harlow's pitting modeling theories, the power law model and the particle-induced pitting corrosion models. Two assumptions are taken in these models:

- a) The pit shape is hemispherical and maintains through the development of pitting;
- b) The pit grows at a constant volumetric rate.

Thus, for a hemispherical pit of depth a_p that grows at a constant volumetric rate (V), there is:

$$\frac{dV}{dt} = 2\pi a_p^2 \frac{da_p}{dt} \quad (2)$$

And with Faraday's law:

$$\frac{dV}{dt} = \frac{MI_p}{nF\rho} \quad (3)$$

where M is the molecular weight of the material, I_p is the pitting current, n is the valence, F is the Faraday's constant, and ρ is the density (Harlow and Wei, 1994). It can be seen that the definition of pitting current I_p is the key element in the pitting corrosion modeling, which is the effective galvanic current between the constituent particles and the matrix exposed to the corrosive environment (Liao and Wei, 1999).

3.1 Power law based simplified model

When pitting corrosion occurs at an exposed surface, the size of the pit a_p is typically described by a power law as a function of pitting time t (Ghiocel and Tuegel, 2004), as:

$$a_p = Bt^{1/m} \quad (4)$$

where B and m are empirically determined parameters and m usually has a value between 2 and 4. This equation represents how the maximum of the distribution of the pit depth changes with time. Following the power law, Harlow and Wei (1994) has developed a simplified model that exhibits temperature dependence, where the pitting current I_p is defined as:

$$I_p = i_{p0} e^{\frac{\Delta H}{RT}} \quad (5)$$

ΔH is the activation enthalpy; R is the universal gas constant; T is the absolute temperature; and i_{p0} is the pitting current coefficient. From the above equations and implementing simple integration, we can derive the pit size a_p as a function of pitting time t :

$$a_p = \sqrt[3]{\frac{3M}{2\pi nF\rho} i_{p0} e^{\frac{\Delta H}{RT}t} + a_0} \quad (6)$$

with a_0 being the initial pit size (model I).

Using this setup and input data from (Sriraman and Pidaparti, 2009) of 2024-T3 alloy and assuming the aircraft is on ground (T approximated as 300K), and the alloy exposed to a 0.5 M NaCl solution, the estimate of the pit size as a function of pitting time is shown in Figure 3a. The markers represent the results reported in the literature (Sriraman and Pidaparti, 2009), in good agreement with the model results. In the derivation, ΔH is taken at 40 kJ/mole, which is a

typical value for aluminum alloys (Harlow and Wei 1994). We also run the model at various temperatures of 20°C, 25°C, 30°C, 35°C, and 40°C as shown in Figure 3b. Clearly the temperature promotes the pit growth.

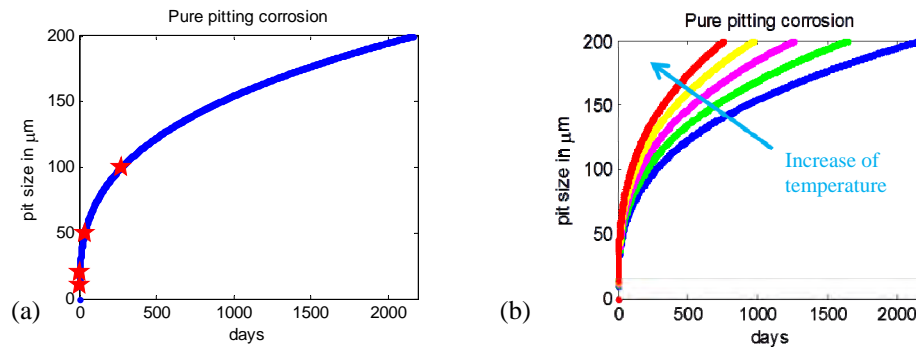


Figure 3 Pit size estimates as function of pitting time. (a) Pure pitting and (b) influence of temperature.

The result shown in Figure 3a indicates that pure pitting corrosion is a very slow process. With the given conditions, it takes around 2000 days for it to grow up to 200 μm. Since pit initiation and growth is also known to be affected by the fatigue stress simultaneously added to the process (Sriraman and Pidaparti, 2009), a suitable stress-dependent factor can be added to the model. According to (Sriraman and Pidaparti, 2009), the pit size is found to be directly correlated to the stress amplitude σ_a that takes the form of 1.01^{σ_a} based on experimentation data of 2024-T3. The factor indicates that the stress is promoting the pitting. The fatigue assisted pitting model result is given in Figure 4 with a stress loading of 180 MPa. In comparison to the pure pitting, the pitting is significantly accelerated, taking only 1 day to reach 100 μm. The markers represent the results reported in the literature (Sriraman and Pidaparti, 2009), in good agreement with the model derived here.

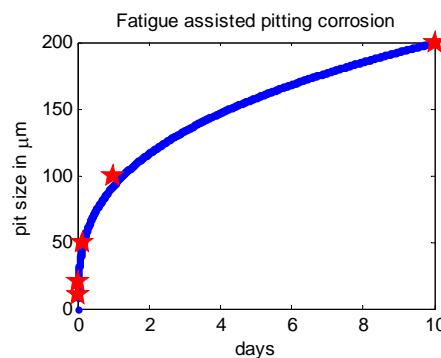


Figure 4 Fatigue assisted pitting.

3.2 Microstructure based pitting models

The previous simple model is good for characterizing pitting corrosion around an isolated particle or a small cluster of particles at the alloy surface. However its capability to describe the development and growth of a severe corrosion pit is limited and problematic. Recall in the particle induced pitting theory, pit growth is considered to be sustained by galvanic current from coupled constituent particles with the alloy matrix when both are exposed to the deleterious environment at the surface of the growing pit (Wei, 2001)(Harlow and Wei, 2009). Hence once the dissolution around the surface particle separates and electrically disconnects it from the matrix, using “constant” pitting current in the phenomenology loses its physical underpinning. More realistic models are needed.

Based on Wei’s particle-induced pit growth theory (Wei, 2001) (Harlow and Wei, 2009), a simple physically based model that involves the alloy microstructural characteristics as well as the electrochemical conditions is developed. The model assumes that the pit growth is initiated from the cluster (defined as a group of constituent particles) at the external surface and sustained by the galvanic current from constituent particles that are exposed at the surface of a growing pit.

In this model, the pitting current is considered to be associated with the limiting cathodic current densities $(i_{co})_k$ on individual constituent particles at the pit surface, as:

$$I_p = \sum_{k=1}^{n_{pt}} (i_{co})_k (2\pi a_{pt}^2)_k \quad (7)$$

Here n_{pt} is the total particle number at the pit surface; a_{pt} is the radius of the k^{th} particle which is assumed to take hemispherical shape for simplicity; and $(2\pi a_{pt}^2)_k$ represents the surface area of the particle that is exposed to the electrolyte. The limiting cathodic current density depends on the composition of the individual constituent particles and electrochemical conditions within the pit, both of which can change over time. For simplicity, we *assume*: (1) the limiting cathodic current density is identically distributed over particles, (2) the particles take an average radius of \bar{a}_{pt} , and (3) are uniformly distributed with an average density of \bar{d}_{pt} . Then the pitting current becomes:

$$(a) I_p = i_{co} \cdot n_{pt} \cdot (2\pi \bar{a}_{pt}^2) \text{ or } (b) I_p = i_{co} \cdot (\bar{d}_{pt} \cdot 2\pi \bar{a}_p^2) \cdot (2\pi \bar{a}_{pt}^2) \quad (8)$$

It shows that the pitting current as well as the galvanic dissolution of the alloy matrix through its coupling with the particles is progressively increasing by pitting. Using the pitting currents derived in Eq. (8), now the pit size can be obtained:

$$\text{Using (8a)} \quad a_p = a_0 + \frac{M}{n\rho F} i_{co} \bar{d}_{pt} (2\pi \bar{a}_{pt}^2) t \quad (9)$$

$$\text{Using (8b)} \quad a_p = \sqrt[3]{a_0^3 + \frac{3M}{n\rho F} \bar{a}_{pt}^2 i_{co} \int n_{pt}(t) dt} \quad (10)$$

Given the pitting setup in Section 3.1, the estimate using (a) (model II) for pitting time of 384 hours is given in Figure 5a ($a_{pt} = 5 \mu\text{m}$, $i_{co} = 200 \mu\text{A}/\text{cm}^2$, $a_0 = 14 \mu\text{m}$, $\bar{d}_{pt} = 1330 \text{ particles}/\text{mm}^2$) and the estimate using Eq. (10) (model III) in Figure 5b. In most applications, the particle size can range from 1 to 30 μm . Meaningful density is related to the particle size and would cover inter-particle distance of 2~4 particle radius. For limiting cathodic current density, it depends on the composition of the particle and electrochemical conditions within the pit, and can range from 40 to 600 $\mu\text{A}/\text{cm}^2$ (Wei, 2001) (Harlow and Wei, 2009). The output of model II and III agree well with the work presented in the literatures (Wei, 2001) (Harlow and Wei, 2009).

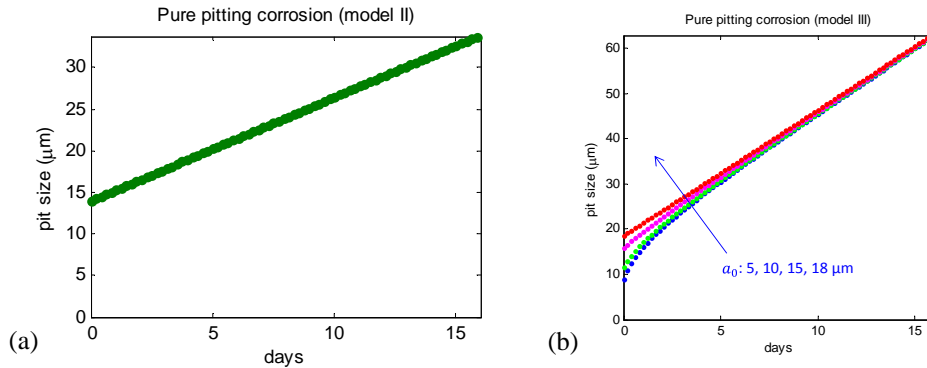


Figure 5 Pit size estimates based on microstructures and electrochemical conditions: (a) Using particle density (model II); (b) using particle numbers (model III)

4 FATIGUE LIFE OF PRE-CORRODED ALUMINUM ALLOY MODELING

For the pre-corroded alloy fatigue life prediction, it is believed the fatigue life is essentially governed by the size of the maximum pit size at the surface and the subsequent crack growth (Wei 2001). The crack nucleation time, if present at all, can be reasonably neglected (Wei 2001). The initial pit is assumed to be equivalent to a semi-circular crack and the crack begins growth from the first loading cycle. In this study, the crack propagation model is based on the well-known Paris law (Sriraman and Pidaparti, 2009):

$$\frac{da}{dN} = C(\Delta K)^m \quad (11)$$

Where a is the crack size, N is the fatigue life, C is the fatigue coefficient, m is the fatigue exponent, and $\Delta K = \beta \sigma_a \sqrt{\pi a}$ where β is the geometry factor and σ_a is the loading applied. Although the Paris law is not truly applicable for small crack growth, it is taken for simplicity. Also it is assumed the crack growth is primarily stress driven and the crack closure effect is negligible (Sriraman and Pidaparti, 2009). The crack growth life including the short crack growth and the long crack growth to fracture is taken as:

$$N = \frac{a_s^{\frac{1-m_1}{2}} - a_{tr}^{\frac{1-m_1}{2}}}{\left[\frac{m_1}{2} - 1\right] C_1 (2\beta_1 \sigma_a \sqrt{\pi})^{m_1}} + \frac{a_{tr}^{\frac{1-m_2}{2}} - a_f^{\frac{1-m_2}{2}}}{\left[\frac{m_2}{2} - 1\right] C_2 (2\beta_2 \sigma_a \sqrt{\pi})^{m_2}} \quad (12)$$

Here a_s is the short crack length which will be replaced by the initial pit size in the corrosion fatigue model; a_{tr} is the transition length from short to long crack; and a_f is the final critical crack length, given by $a_f = (K_c / 1.12 / \sigma_a)^2 / \pi$ where K_c is the material fracture toughness. Using the data from (Sriraman and Pidaparti, 2009), the fatigue life predictions for the model I and II developed in Section 3 are acquired and shown in Figure 6.

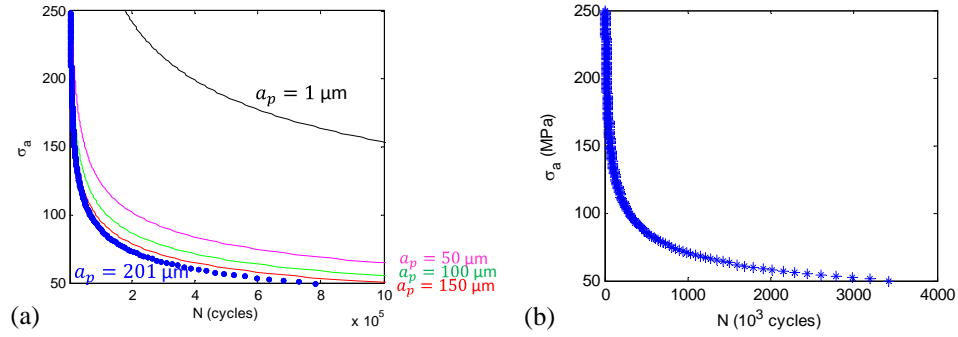


Figure 6 Fatigue life prediction of pre-corroded 2024-T3. (a) Life prediction of model I at various pit size showing that fatigue life is significantly reduced with enlarged pit size; (b) life prediction of model II with a pit size of 70 μm ($\sigma_a=250$ MPa)

To have a better understanding of the corrosion influence on fatigue life, the pitting and loading process are combined and a direct relation between the pit size and the life cycles can be achieved (Figure 7). It shows that as the pit grows, the fatigue life is exponentially reduced.

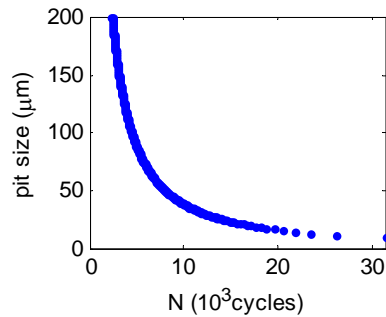


Figure 7 Pitting influence on fatigue life

5 CONCLUSIONS

Corrosion fatigue has serious impacts on the continued safe operation of aircraft. US Air Force, US Navy and the FAA have guidelines on how aircraft should be designed and maintained to minimize the risk of failure from fatigue damage (Ghiocel and Tuegel, 2004). However, there are limited instructions regarding corrosion, noting that each part of the aircraft has to be “suitably protected against deterioration or loss of strength in service due to any cause, including weathering, corrosion and abrasion”. A framework to assess the effect of corrosion in combination with fatigue on structural integrity has been a dire need and under development for some time. Risk of failure caused by corrosion fatigue is of primary interest to the aircraft fleet management. The literature review and study provided in this paper presented several well-known pitting corrosion fatigue models and the key aspects of assessing pitting corrosion fatigue in aluminum alloy aircraft structural components. It is seen that such physics-driven models can reflect both loading and environmental influences in the overall corrosion fatigue process. The future work is planned on obtaining experimental data and validation of customized predictive models.

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